Transport Properties, Thermal Response, and Mechanical Reliability of Thermoelectric Materials and Devices for Automotive Waste Heat Recovery

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2013 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting
Arlington, VA
14 May 2013

Project ID:
pm012_wereszczak_2013_o

Overview

Timeline

- Project start: October 2006
- CRADA start: March 2009
- Project end date: Nov 2013
- Percent complete: 93%

Budget

- Total project funding

	FY09	FY10	FY11	FY12	FY13
DOE	$300k	$300k	$300k	$375k	$340k
Marlow	$75k	$150k	$150k	$150k	$150k

Barriers

- Barriers addressed
  - 2/3 chemical energy in automotive fuel is rejected to atmosphere as waste heat
  - Thermomechanical stresses must be managed and thermoelectric (TE) material strength improved to exploit TE devices
  - TE materials are inherently brittle and susceptible to thermal-induced fracture
- Targets*
  - 5000h life or 10 yr or 150k mile lifetime
  - Brittle bulk materials must survive thermal and mechanical stresses for life

Partners

- Marlow Industries (CRADA)
- General Motors (indirectly)
- International Energy Agency, IEA, (14 participants from 7 countries)

* "A Science-Based Approach to Development of Thermoelectric Materials for Transportation Applications, Office of FreedomCAR and Vehicle Technologies, August 8, 2007.

Objectives

1. **CRADA with Marlow (44% of project)**
   - Measure needed transport, thermal, and mechanical properties of Marlow's candidate thermoelectric materials (TEMats) that are under consideration for automotive waste heat recovery and cooling applications.
   - Measure needed properties of other material constituents used in thermoelectric devices (TEDs).
   - Develop accelerated test method to assess operational fatigue resistance of TEDs.
2. **International Energy Agency (IEA) collaboration (37% of project)**
   - Coordinate international round-robin testing and measurement of transport properties with the intent to improve their consistency and validity.
   - Promote standardization of test methods pertinent to TEMat characterization.
3. **Cross-cutting R&D (19% of project)**
   - Measure transport, thermal, and mechanical properties of developmental TEMats under consideration for automotive waste heat recovery.
   - Compose book chapter on the mechanical evaluation of TEMats.
   - Advanced characterization of TEMat using high temperature X-ray diffraction and scanning transmission electron microscopy (STEM).

Milestones

- **FY12:**
  - **Measure mechanical, thermoelastic, and thermoelectric properties of Marlow-fabricated TEMats to enable operation up to 500°C.** ***Completed.***
  - **Complete report of international round-robin test results on Marlow bismuth telluride to IEA-AMT and initiate a new high temperature thermoelectric round-robin measurement on PbTe or skutterudite ranging between 20-500°C.** ***Completed.***
- **FY13:**
  - **Complete IEA-AMT Annex VIII international round-robin study on TE material transport and thermal property testing to 500°C and form team for follow-up round-robin TE module efficiency testing.** ***30 Sep 2013 - on track.***
  - **Complete adhesion evaluation of TE device metallization and continue to generate transport, thermoelastic, and mechanical properties of high-temperature-capable TEMats as part of Marlow-ORNL CRADA.** ***30 Sep 2013 - on track.***

Technical Approach

- **CRADA with Marlow**
  - **Property measurement – Marlow TEMats.** Measure electrical conductivity, Seebeck coefficient, heat capacity, thermal conductivity, Young's Modulus, Poisson's ratio, coefficient of thermal expansion, and mechanical strength as a function of temperature of candidate Marlow TEMats.
  - **Supportive materials.** Provide supportive characterization of the other material constituents (e.g., metallizations, diffusion barriers) used in Marlow's TEDs.
  - **TED testing.** Use operational deformation field to guide development of accelerated fatigue tests of TEDs.
- **IEA collaboration**
  - **Property testing.** Coordinate international round-robin testing and measurement of transport properties to improve their consistency and validity.
  - **Standardization.** Use round-robin results to recommend test standardizations.
- **Cross-cutting R&D**
  - **Property measurement - TEMats.** Measure electrical conductivity, Seebeck coefficient, heat capacity, thermal conductivity, Young's Modulus, Poisson's ratio, coefficient of thermal expansion, x-ray diffraction, and mechanical strength as a function of temperature of candidate TEMats made by other companies and universities.
  - **Reporting.** Compose book chapter on mechanical evaluation of TEMats.

Technical Accomplishments – 1 of 12

Overview of Year's Accomplishments:

- **Mechanical testing of skutterudite TEMats**
- **Evaluations of material constituents used in TEDs**
- **Initial development of accelerated fatigue test method**
- **Neutron diffraction used to estimate residual stresses in prototype skutterudite module legs**
- **Coordinated international round-robin testing, measurement of transport properties, and developed test procedures**

Proposed concept for thermoelectric-device waste heat recovery

Technical Accomplishments – 2 of 12

Why is Mechanical Strength Important to TEMats?

$$R_{Therm} = \frac{S_{Tens}(1-\nu)\kappa}{CTE \bullet E}$$

Kingery, J. Am. Cer. Soc., 38:3-15 (1955).

R_{Therm} = Thermal resistance parameter (the larger the better)
S_{Tens} = Tensile stress or strength
ν = Poisson's ratio
κ = Thermal conductivity
CTE = Coefficient of thermal expansion
E = Elastic modulus

Griffith Criterion

$$S_{Tens} = \frac{K_{Ic}}{Y\sqrt{c}}$$

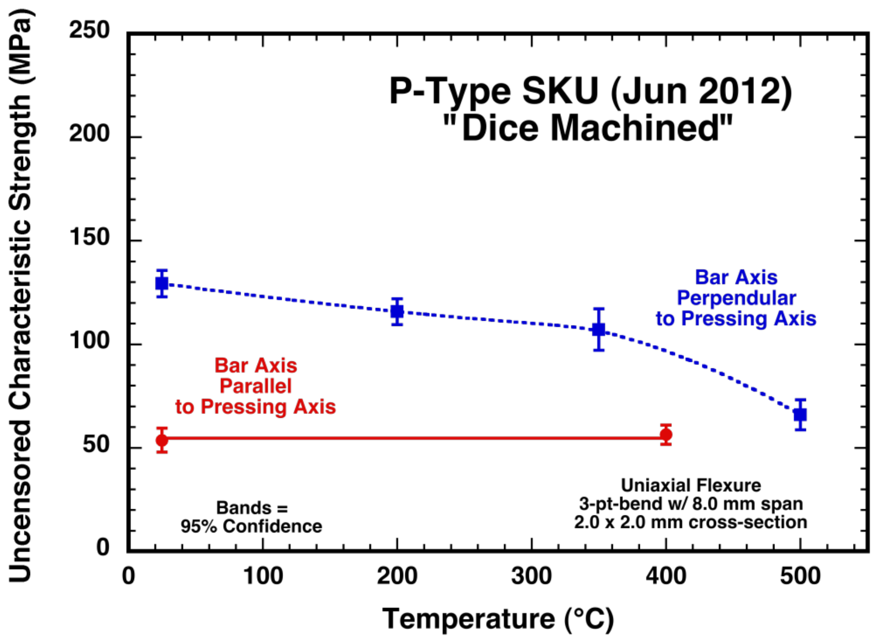
KIc = Fracture toughness
Y = Crack shape factor
c = Griffith flaw size

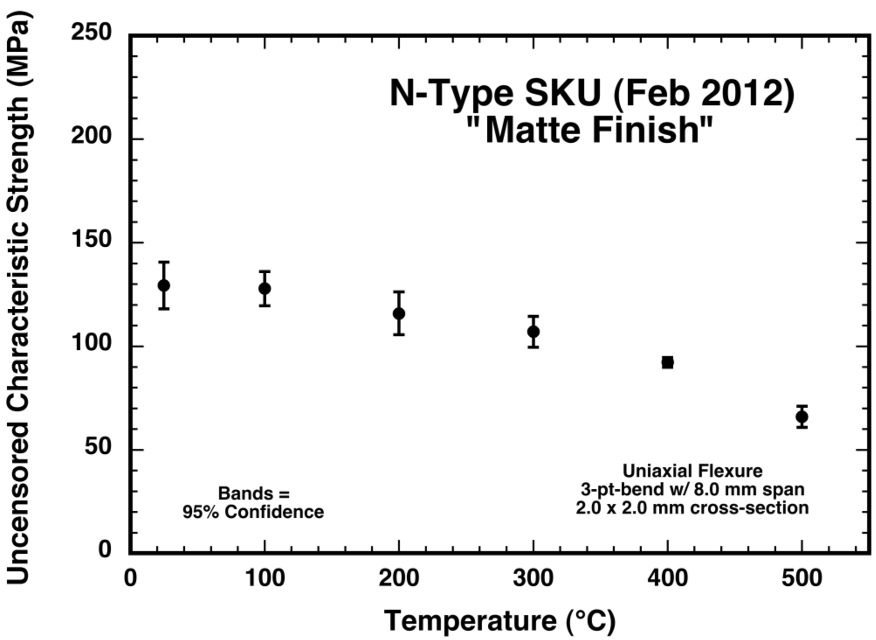
Tensile Strength << Compressive Strength
Manage tensile stress for conservative design

Must seek to minimize c!

Technical Accomplishments – 3 of 12

Strength of FY12-Vintage Skutterudites; strength is a function of temperature

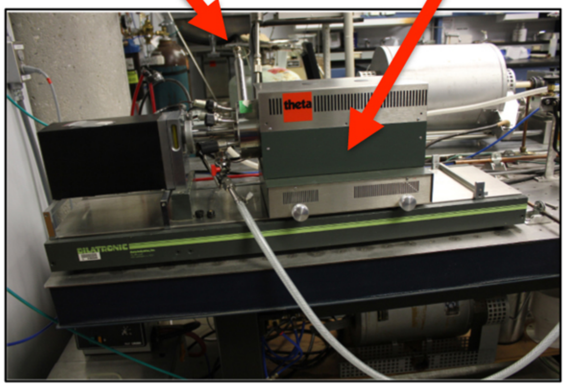


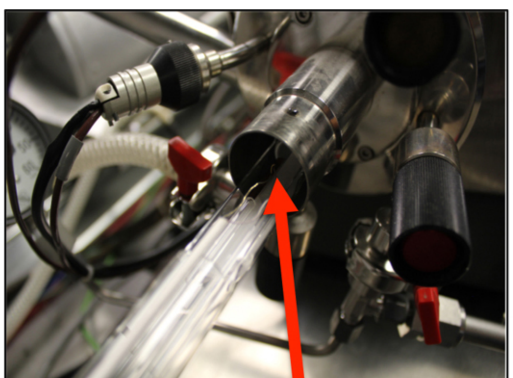


Technical Accomplishments – 4 of 12

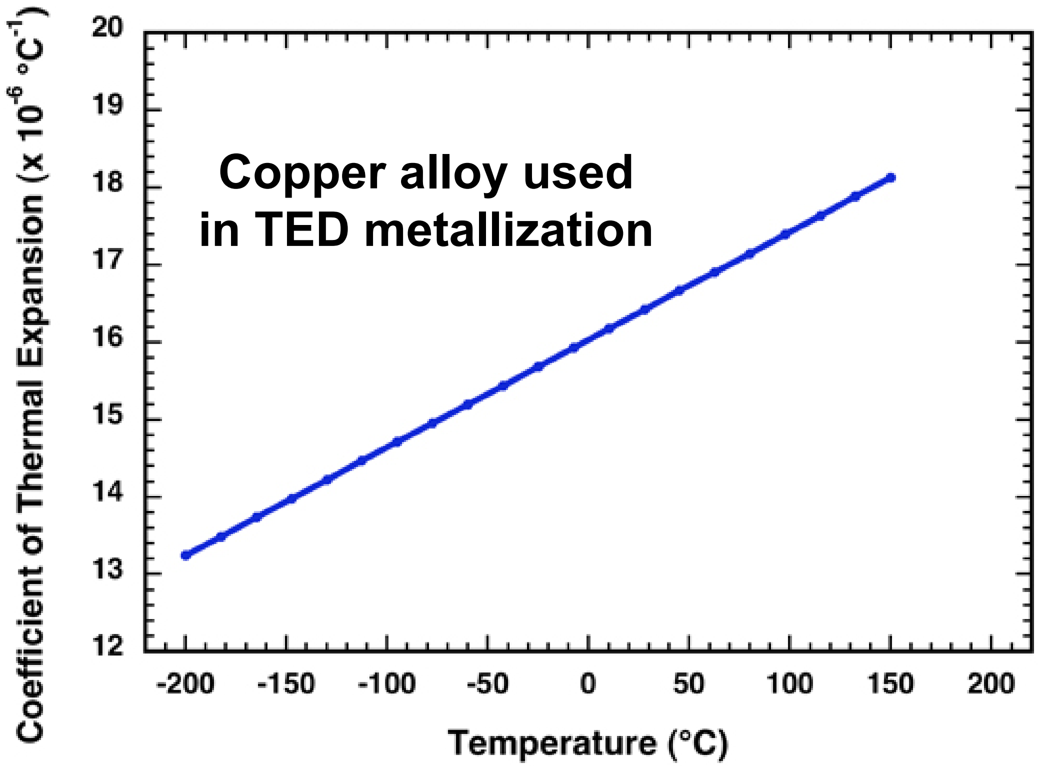
Example of TED material constituent characterization: CTE measurement over a wide temperature range

Port for liquid helium **Cryostat**





Push rods for sample and reference

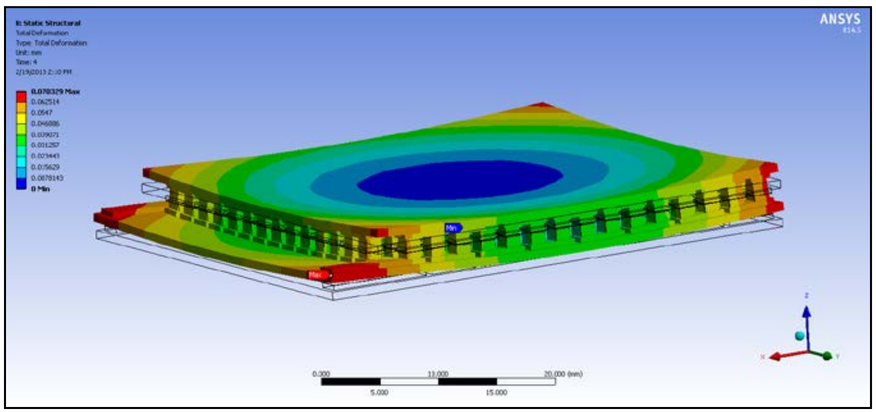


Technical Accomplishments – 5 of 12

Accelerated Fatigue Testing Development

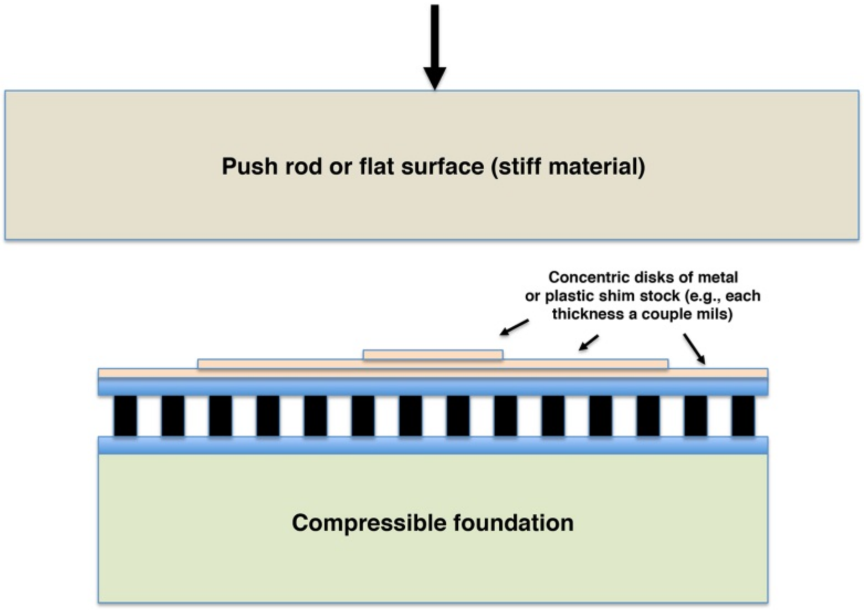
Predicted Deformation

Biaxial and axisymmetric deformation caused by temperature gradient



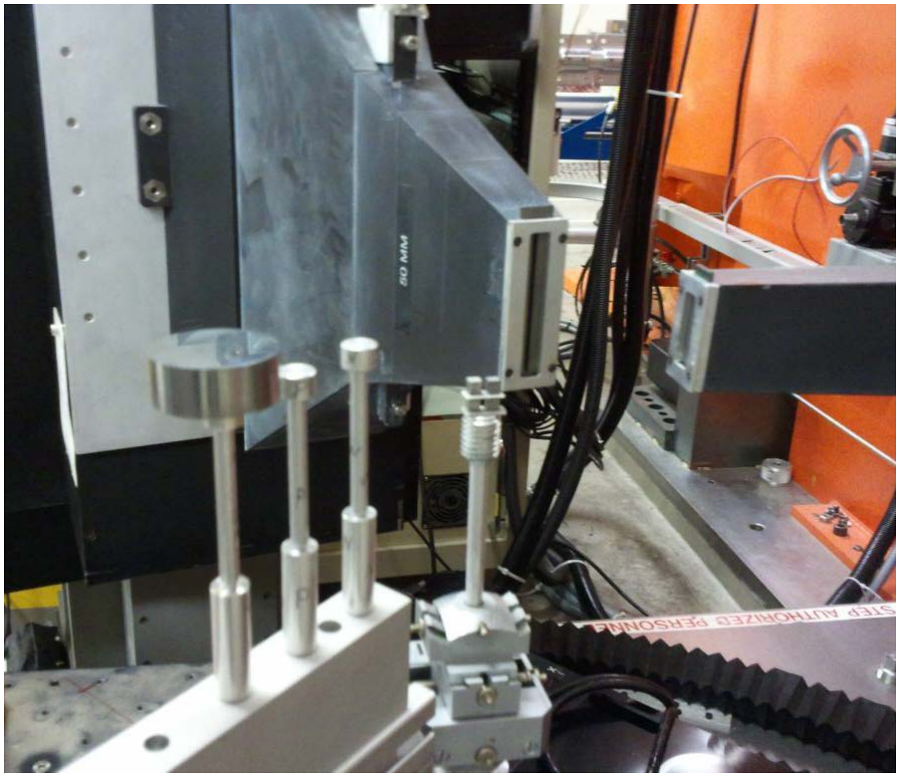
Experimental

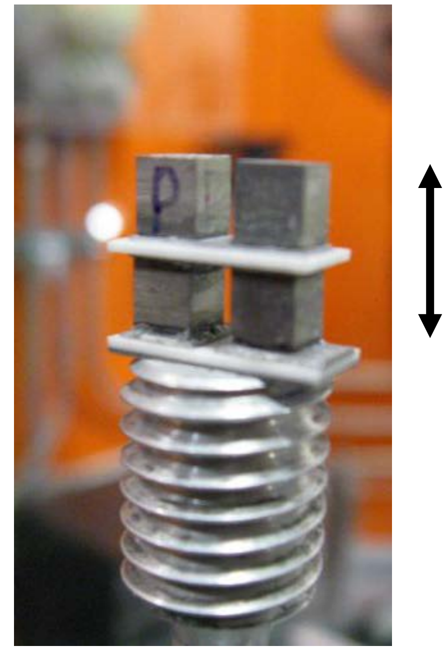
The use of concentric shims coupled with compression-compression loading can potentially mimick deformations due to thermal cycling. Rapid loading can enable accelerated testing.



Technical Accomplishments – 6 of 12

Measured Residual Strains Using Neutron Diffraction



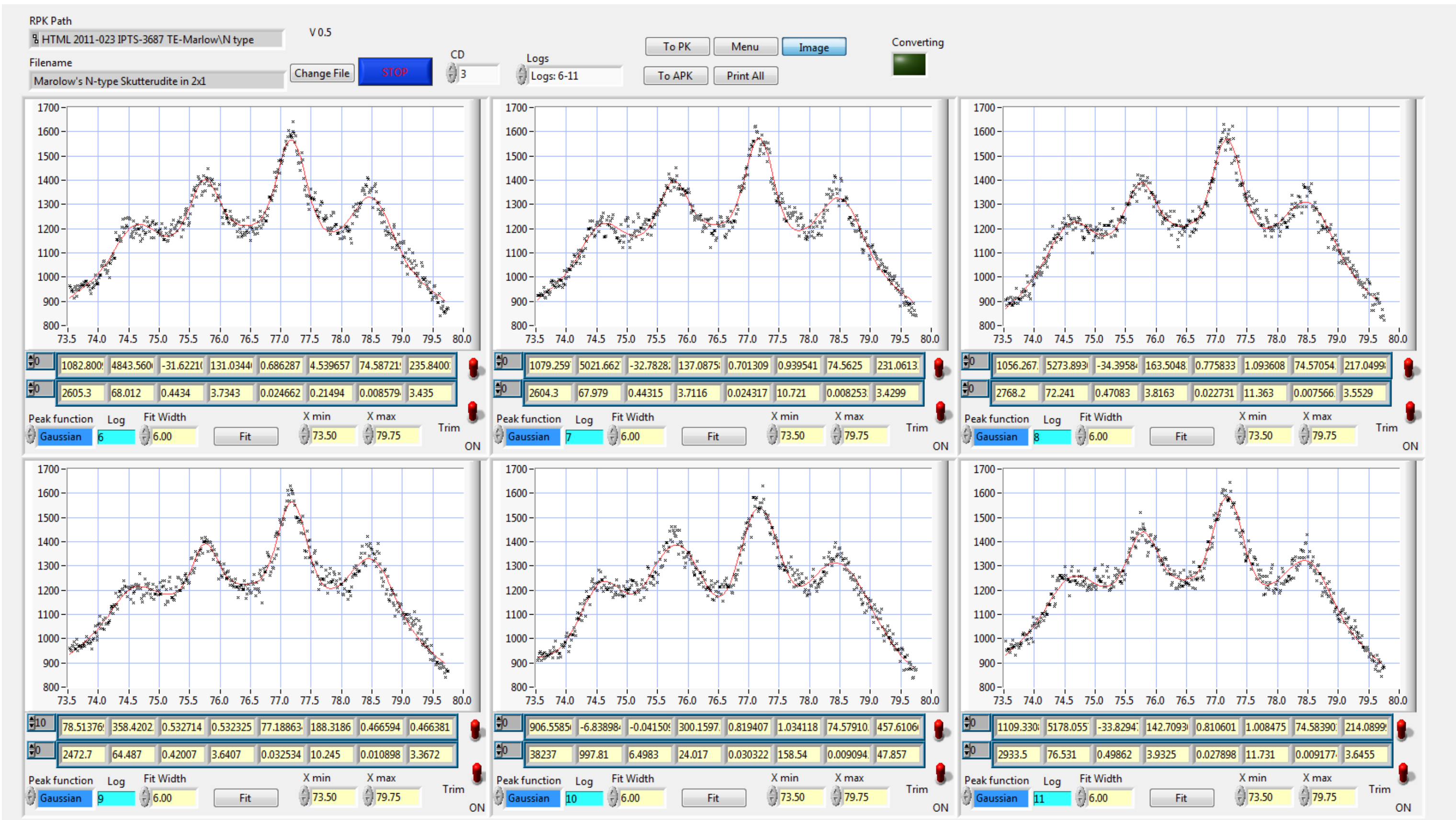


3mm x 3mm x 0.5mm Gauge Volume

HFIR set up: Marlow/GM skutterudite module
10 scans in the Z-direction were performed to measure residual strain

Technical Accomplishments – 7 of 12

Identified Positional Dependence of Residual Strain

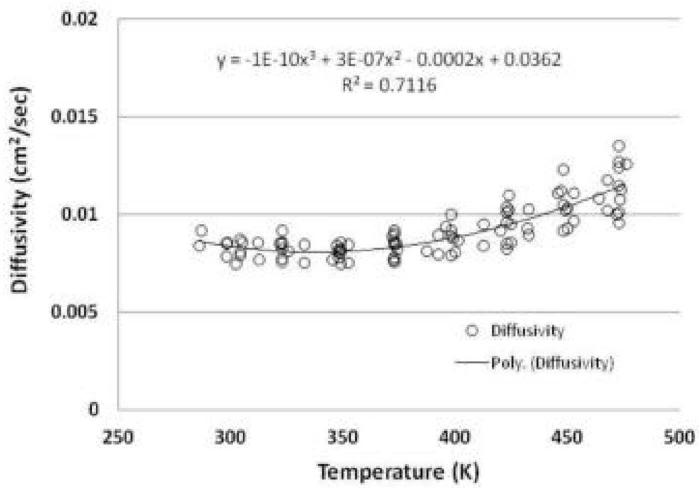


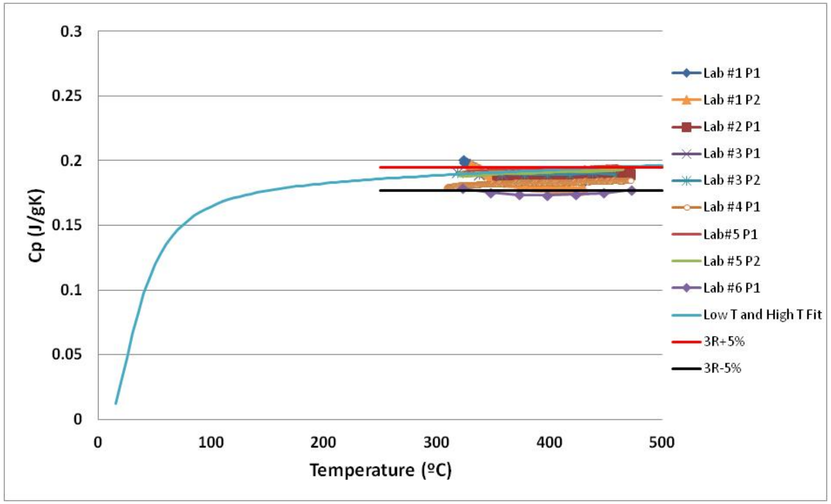
Technical Accomplishments – 8 of 12

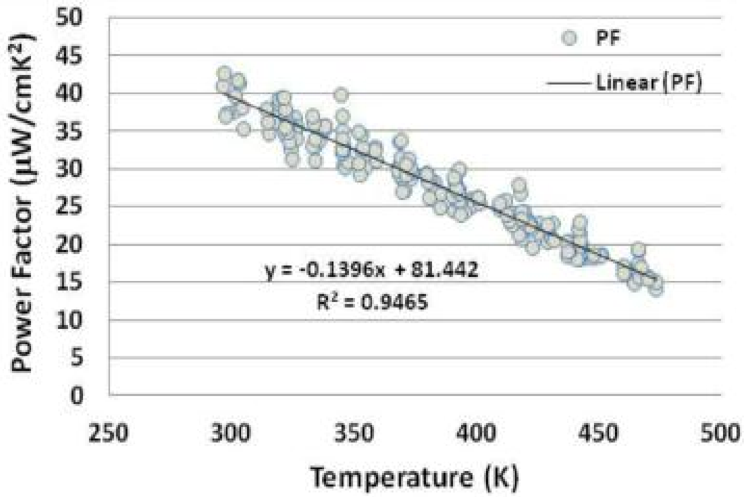
IEA-AMT Annex VIII Support and Participants

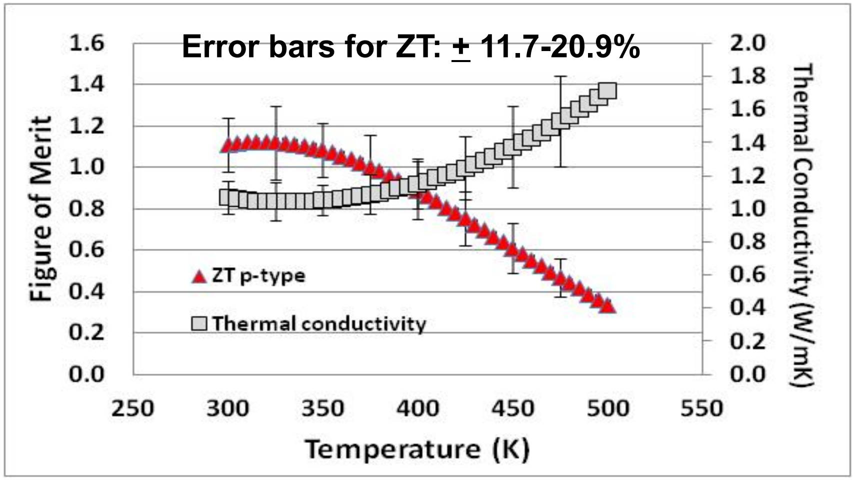
- **IEA-AMT Thermoelectric Annex**
  - **Annex lead: Oak Ridge National Laboratory (H. Wang)**
  - **USA: Clemson (T. Tritt, S. Zhu); Marlow (J. Sharp); Corning (A. Mayolet, C. Smith, J. Senawiratne) and ZT-Plus (F. Harris)**
  - **China: SICCAS (SQ Bai, L. Chen)**
  - **Canada: Natural Resource Canada (J. Lo); University of Waterloo (Holger Kleinke); University of Quebec at Chicoutimi (Laszlo Kiss)**
  - **Germany: Fraunhofer IPM (H. Böttner, J. König)**
  - **International Observer: Japan: AIST (R. Funahashi)**
  - **International Observer: Korea: KERI (H. W. Lee)**
- **New Participants for High Temperature Round-robin: NPL (UK); GM Global R&D (USA) and GMZ Energy (USA)**
- **14 participants from 7 countries**

Final Calculation of ZT: IEA P-type Sb_2Te_3-Bi_2Te_3









Since thermal diffusivity and specific heat are measured separately, they must all be reported to show how thermal conductivity is obtained.

Technical Accomplishments – 10 of 12

Round-robin 3 on Half-Heusler Thermoelectrics in Automotive Exhaust Temperature Range (to 500°C)

- **Half-Heusler composition: $Zr_{0.5}Hf_{0.5}CoSb_{0.8}Sn_{0.2}$ (n-type)**
- **GMZ Energy volunteered their half-heusler materials for the round-robin effort (March 2012)**
- **Materials processed and machined at GMZ Energy and first set measurements completed in May 2012**
- **Round-robin: GMZ -> Germany -> China -> US (ORNL, GM) -> NPL -> Canada**
- **Samples at NPL as of February 2013**

Technical Accomplishments – 11 of 12

Round-robin summary:

- **IEA-AMT is addressing the important issue of measurement and standardization of thermoelectric properties**
- **Significant measurement issues were observed, especially in specific heat measurements**
- **Good agreements in Seebeck coefficient and electrical resistivity in round-robin No. 2**
- **Thermal diffusivity in good agreement except for one test**
- **Overall errors for ZT are from $\pm$ 12% to 21%**
- **IEA-AMT topical report published and two journal papers published based on round-robin results**

Technical Accomplishments – 12 of 12

Many of the results and experiences from this project's history will be captured in a new book and one of its book chapters

Thermoelectric Technology for Electrical Power Generation from Waste Heat
Applications, Systems, Devices, and Materials
Gregory P. Meisner, James R. Salvador, Jihui Yang, editors

Thermoelectric Technology for Electrical Power Generation from Waste Heat

Chapter 16
Mechanical Response of Thermoelectric Materials

Andrew Wereszczak, Oak Ridge National Lab, and Eldon Case, Michigan State University

1. Introduction
    - A. The thermoelectric leg unit cell
    - B. Stress analysis of the service thermal gradient
    - C. Interpretation and management of tensile stress
        - I. Maximum Principal stress failure criterion
        - II. Brittle material component design
            - a. Rationale
                - i. Tension-compression anisotropy
                - ii. Size-scaling of tensile failure stress
            - b. The algorithm and its needed input
2. Properties, Characteristics, and Test Methods
    - A. Mechanical
        - I. Elastic modulus and Poisson's ratio
        - II. Strength
            - a. Strength; not a material property
            - b. Statistical analysis and effective size
            - c. Testing leg geometry and non-standardized testing
            - d. Flexure testing
                - i. Uniaxial
                - ii. Biaxial
            - e. Flaws and strength-limitation
                - i. Flaw types and strength data censoring
                - ii. Dicing and machining quality
                - iii. Process maturity; flaw type transformation
            - f. Proof testing
        - III. Secondary but informative properties and characteristics
            - a. Fracture toughness
            - b. Compressive strength
            - c. Hardness
    - B. Thermal
        - I. Shock and gradient
        - II. Diffusivity, conductivity, and heat capacity
        - III. Coefficient of thermal expansion
        - IV. Thermal fatigue, thermoelastic and energy balance approaches
    - C. Material anisotropy
        - I. Symmetrical transverse isotropy (caused by unidirectional pressing)
        - II. Anisotropy relative to leg geometry
3. Material Non-Equilibrium
    - A. Excessive temperature
    - B. Oxidation
    - C. Thermal fatigue
    - D. Bloating
4. Case Study: Materials TBD [or Appendix of properties?]
5. References
6. Acknowledgments

Collaborations

- **CRADA with Marlow Industries.**

- **General Motors. Marlow is a contractor to General Motors on the DOE-funded program "Development of Cost-Competitive Advanced Thermoelectric Generators for Direct Conversion of Vehicle Waste Heat Into Useful Electrical Power". Therefore ORNL's CRADA with Marlow indirectly benefits General Motors. Others potentially and indirectly benefitting from our CRADA with Marlow on that GM-led program include DANA, Delphi, Eberspaecher Exhaust Technology, and Molycorp.**

- **IEA collaborations: Clemson University, Marlow, Corning, ZT-Plus, GMZ Energy, SICCAS (China), CANMET(Canada), University of Waterloo (Canada), University of Quebec (Canada), Fraunhofer IPM (Germany), NPL (UK), AIST (Japan), and KERI (South Korea).**

Future Work

- Continue collaboration with Marlow Industries to contribute to the reliability improvement of their candidate TEMats and TEDs
- Continue to mechanically evaluate constituents (e.g., metallizations, diffusion barriers, etc.) in TEDs
- Develop and demonstrate accelerated fatigue test method of TEDs
- Complete bookchapter on *Mechanical Response of Thermoelectric Materials* for the book Thermoelectric Technology for Electrical Power Generation from Waste Heat Applications, Systems, Devices, and Materials, Eds. G. P. Meisner, J. R. Salvador, and J. Yang, Springer-Verlag, in preparation, 2013.
- Complete measurement round-robin No. 3 up to 500°C for automotive waste heat recovery
- Conduct survey and initiate IEA study on thermoelectric module efficiency tests

Summary

- **<u>Relevance:</u>** **thermoelectrics are exploitable for automotive waste heat recovery for on-board power generation**
- **<u>Approach:</u>** **characterize TEMats and TEDs and promote transport and thermal test standardizations**
- **<u>Collaborations:</u>** **a primary TEMat and TED manufacturer (Marlow), an automotive OEM, and several other institutes and universities.**
- **<u>Technical Accomplishments:</u>**
  - **Characterizations of TEMats and other material constituents in TEDs**
  - **Initial development of accelerated fatigue test method**
  - **Neutron diffraction used to estimate residual stresses**
  - **IEA round-robins of property measurements (14 participants from 7 countries)**
  - **Heat capacity measurement found to be the major source of error for ZT**
- **<u>Future work</u>:**
  - **Development of accelerated fatigue test method**
  - **IEA round-robin on transport properties and initiate study on efficiency test**
  - **Complete book chapter on mechanical evaluation of TEMats**